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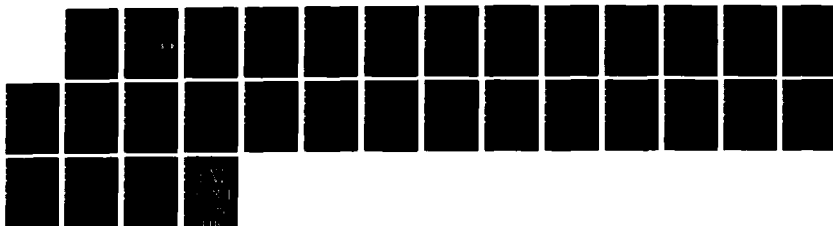
INFRARED AND ULTRASONIC SPECTRA OF SODIUM THIOCYANATE
AND LITHIUM THIOCYA. (U) POLYTECHNIC INST OF NEW YORK
FARMINGDALE DEPT OF CHEMISTRY D SAAR ET AL. JAN 86
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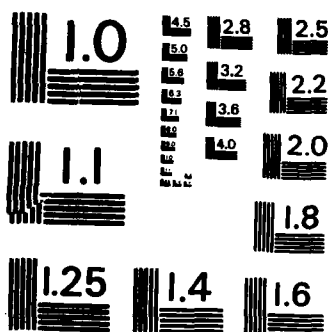
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER <i>ARO 21758.4-CH</i>	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) "Infrared and Ultrasonic Spectra of Sodium Thiocyanate and Lithium Thiocyanate in Tetrahydrofuran"		5. TYPE OF REPORT & PERIOD COVERED Technical
		6. PERFORMING ORG. REPORT NUMBER 8
7. AUTHOR(s) D. Saar and S. Petrucci		8. CONTRACT OR GRANT NUMBER(s) DAAG29-85-K-0051
9. PERFORMING ORGANIZATION NAME AND ADDRESS Polytechnic Institute of New York Department of Chemistry Long Island Center, Farmingdale, NY 11735		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS N/A
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE January 1986
		13. NUMBER OF PAGES 27
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the authors and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Infrared spectra of sodium thiocyanate solutions and of lithium thiocyanate solutions in tetrahydrofuran (THF) in the wavenumber range 2000-2200 cm^{-1} are reported. The digitized spectral envelope, which is due to the out of phase stretch of the SCN anion, is quantitatively described by the sum of three Gaussian-Lorentzian product functions. The three spectral bands are assigned respectively, to the N-bonded ion pairs ($\sim 2057 \text{ cm}^{-1}$ for NaNCS, $\sim 2064 \text{ cm}^{-1}$ for LiNCS), to the dimers or quadrupoles ($\sim 2043 \text{ cm}^{-1}$ for		

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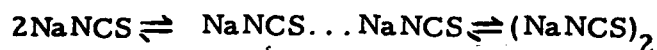
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 (NaNCS)₂), 2040/cm⁻¹ for (LiNCS)₂, and tentatively to triple ions (2074/cm⁻¹ for sodium thiocyanate, 2086/cm⁻¹ for lithium thiocyanate). The maximum absorbances per unit length of cell are expressed as a function of concentrations by cubic polynomial functions.

✓ Ultrasonic spectra for sodium thiocyanate solutions in THF in the frequency range 0.5-400 MHz are described by the sum of two Debye relaxation functions. The ultrasonic spectra for sodium thiocyanate in THF are interpreted as due to a two step process:



depicting the two steps dimerization of the ion pair NaNCS, the intermediate being a solvent separated species. For lithium thiocyanate solutions in THF, the ultrasonic spectra are described by a single Debye relaxation function, and interpreted by the dimerization scheme $2\text{LiNCS} \rightleftharpoons \text{LiNCS} \dots \text{LiNCS}$, the product of the reaction being mostly a solvent separated species, the "contact" species being probably in lesser amounts than for (NaNCS)₂ in accordance with the evidence from the infrared spectra.

✓ The limitations of the infrared method in giving reliable formation stoichiometric constants in media of low permittivity are discussed. The advantage of combining the structural information from vibrational spectra to the kinetic results of the ultrasonic spectra for a molecular interpretation of the latter ones is reiterated.

Infrared and Ultrasonic Spectra of Sodium Thiocyanate and Lithium Thiocyanate in Tetrahydrofuran

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Abstract

Infrared spectra of sodium thiocyanate solutions and of lithium thiocyanate solutions in tetrahydrofuran (THF) in the wavenumber range $2000\text{--}2200\text{cm}^{-1}$ are reported. The digitized spectral envelope, which is due to the out of phase stretch of the SCN anion, is quantitatively described by the sum of three Gaussian-Lorentzian product functions. The three spectral bands are assigned respectively, to the N-bonded ion pairs ($\sim 2057\text{cm}^{-1}$ for NaNCS, $\sim 2064\text{cm}^{-1}$ for LiNCS), to the dimers or quadrupoles ($\sim 2043\text{cm}^{-1}$ for $(\text{NaNCS})_2$, 2040cm^{-1} for $(\text{LiNCS})_2$, and tentatively to triple ions (2074cm^{-1} for sodium thiocyanate, $\sim 2080\text{cm}^{-1}$ for lithium thiocyanate). The maximum absorbances per unit length of cell are expressed as a function of concentrations by cubic polynomial functions.

Ultrasonic spectra for sodium thiocyanate solutions in THF in the frequency range $0.5\text{--}400\text{MHz}$ are described by the sum of two Debye relaxation functions. The ultrasonic spectra for sodium thiocyanate in THF are interpreted as due to a two step process:



depicting the two steps dimerization of the ion pair NaNCS, the intermediate

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The limitations of the infrared method in giving reliable formation stoichiometric constants in media of low permittivity are discussed. The advantage of combining the structural information from vibrational spectra to the kinetic results of the ultrasonic spectra for a molecular interpretation of the latter ones is reiterated.

Recently there has been a renewed interest,¹ after the classical work of Fuoss and Kraus² of the thirties, in the association and dimerization of electrolytes in media of low permittivity. The practical relevance of these systems, especially lithium salts in ethereal solutions, is due to their use in the construction of secondary batteries. The knowledge of the state of association of the electrolyte and of the lifetime of the complex species is essential for the optimal choice of solvent and electrolyte. Despite recent advances in application of transport theories of electrolytes,³ theoretical new expressions for the formation constant of dimers ion-pairs⁴ and triplets,⁵ our knowledge of the structure of the complex species in solution is scarce or non-existing.

To this end a program by vibrational IR spectra combined to the already existing molecular relaxation dynamic methods (microwave dielectric relaxation and/or ultrasonic relaxation) has been initiated. For the present work the electrolytes sodium thiocyanate and lithium thiocyanate in the solvent THF have been examined. For the IR spectra the intramolecular vibration of the anion,

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specifically the out of phase stretch of the SCN^- anion,⁶ (or, in the group frequency jargon the "CN stretch") and its changes due to molecular environments have been used as a probe to study the molecular complexation of the electrolytes.

Ultrasonic relaxation spectra of the same systems are also reported, using the structural information from the IR spectra, for their interpretation.

Experimental

The IR spectra have been recorded by a Perkin-Elmer 983G spectrometer, using scan times and slit program modes (4 and 16, respectively) slow enough that no spectral distortion was noticed with respect to slower modes. The cells were calibrated by the fringe method⁷ before each collected spectrum. They were demountable Perkin-Elmer cells with 0.05 mm teflon spacers. Both CaF_2 and NaCl windows were used, ensuring independence of the spectra from the material of the windows, hence their inertness to possible dissolution into the liquid. The ultrasonic instrumentation, data collection and method have been described extensively in previous works.⁸ Sodium thiocyanate and lithium thiocyanate (Baker reagents with analysis certificate) were re-dried at $\sim 70^\circ\text{C}$ and 110°C , respectively in vacuo ($\sim 1\text{mm}$), in volumetric flasks until constancy of weight. Solutions were prepared by volume addition of THF (Baker ACS) dried over molecular sieves (5\AA) . The molecular sieves had been dried for many hours at $\sim 140^\circ\text{C}$ and cooled in vacuo. Infrared spectra of the THF product as received, showed a faint band at $\sim 3300\text{cm}^{-1}$ which disappeared after a few days exposure to molecular sieves. This indicated absence of water in this product, within the resolution of the 983G spectrometer set with an ordinate scale of 0.25 in absorbance ($A = 0.0025/\text{minimum division}$).

Results and Calculations

Some of the infrared spectra expressed in absorbance vs. wavenumber (cm^{-1}) are depicted in Figs. 1 and 2. The spectra for sodium thiocyanate show rather dramatically the relative change of the two visible bands with total concentration of electrolyte.

For lithium thiocyanate the satellite band is the one at lower wavenumbers at variance with the case of sodium thiocyanate. Indicating qualitatively a different molecular distribution of the species present for the two electrolytes.

For the quantitative interpretation of the spectra they were digitized with a resolution of 2.5 cm^{-1} (1.25 cm^{-1} near the peaks and shoulders). It is known that Lorentzian functions are particular applicable to gases and Gaussian functions are particularly applicable⁹ to solids in terms of the band shape of vibrational spectra. For the present case the empirical Gaussian-Lorentzian product function already used before¹⁰ has been applied

$$A_j = A_j^0 \left(\exp \left[-\frac{(\bar{\nu} - \bar{\nu}_j)^2}{2\sigma_j^2} \right] \right) \left(1 + \frac{(\bar{\nu} - \bar{\nu}_j)^2}{\sigma_j^2} \right)^{-1} \quad (\text{I})$$

with A_j^0 the absorbance at the center band wavenumber $\bar{\nu}_j$, σ_j the variance $\sigma_j = \frac{(\Delta\nu)_{1/2}}{1.46}$, with $(\Delta\nu)_{1/2}$ the bandwidth at $(1/2)A_j^0$ for each band. For the spectra of the present work it has resulted to be necessary the use of three Gaussian-Lorentzian bands for a quantitative interpretation of the absorbance envelope, hence

$$A = \sum_j A_j \quad (J = 1, 2, 3) \quad (\text{II})$$

The parameters used to interpret the spectra are collected in Table I for all the concentrations of sodium thiocyanate and of lithium thiocyanate investigated in THF. Figs 3 and 4 report representative plots of the digitized spectra for sodium thiocyanate and lithium thiocyanate in THF with the indicated band

components (dashed lines) and their sum (solid lines) describing the absorbance envelope.

Representative plots of the ultrasonic spectra for sodium thiocyanate and lithium thiocyanate in THF are reported in Fig. 5 and Fig. 6. For the case of sodium thiocyanate two Debye processes are necessary to interpret the spectra expressed as excess sound absorptions per wavelength $\mu = (\alpha - Bf^2)u/f$, vs the frequency f . In the above, α is the sound attenuation coefficient, B is the background sound absorption ratio α/f^2 at $f \gg f_I, f_{II}$ with f_I and f_{II} the two relaxation frequencies, $B = (\alpha/f^2)f \gg f_I f_{II}$, u is the sound velocity. Therefore:

$$\mu = 2\mu_I \frac{(f/f_I)}{1 + (f/f_I)^2} + 2\mu_{II} \frac{(f/f_{II})}{1 + (f/f_{II})^2} \quad (III)$$

where μ_I and μ_{II} are the maximum sound excess absorptions for the two Debye processes centered at f_I and f_{II} , respectively.

Table II collects all the calculated relaxation parameters and the sound velocities u for the concentrations investigated for sodium thiocyanate and lithium thiocyanate in THF at 25°C.

Discussion

a) Vibrational spectra

The thiocyanate anion is known to be a potentially ambidentate ligand. It is a linear ion which may ligate through the nitrogen or sulfur atom. The three frequencies of the thiocyanate ion are the out-of-phase stretch ν_1 , with characteristic frequency at 2050 cm^{-1} , the in phase stretch ν_3 with characteristic frequency at 735 cm^{-1} , and the bending (double degenerate) mode ν_2 with frequency $\nu_2 = 480 \text{ cm}^{-1}$. These group frequencies (here used as a jargon in place of the more correct term wavenumber) change characteristically depending on the coordination mode. Specifically, N-bonded complexes cause an increase of

ν_1, ν_2 does not change and ν_3 increases, whereas S-bonded complexes show a larger ν_1 increase but a decrease of both ν_2 and ν_3 both being more diagnostic than ν_1 , in determining the bonding end of the anion. However solvent bands often obscure the ν_2 and ν_3 regions. Previous work¹⁰⁻¹² has established that with "hard" poorly polarizable ions as Na^+ and Li^+ the ion pairs contact complexes are N-bonded with a respective increase of $\sim 8\text{cm}^{-1}$ and $\sim 15\text{cm}^{-1}$ of the center band frequency with respect to the spectroscopically free (ion and outer-sphere ion-paired) SCN^- anion.

On the basis of the above, one would attribute the band at $\approx 2057\text{cm}^{-1}$ for NaNCS and $\approx 2064\text{cm}^{-1}$ for LiNCS in THF (Table I) to contact ion pairs. No free ions or outersphere ion pairs are detectable. Past work in this laboratory¹³ and previous one by Chabanel et al¹² have attributed the band at ~ 2040 to contact dimer ion-pairs or quadrupoles $(\text{NaNCS})_2$ and $(\text{LiNCS})_2$.

One has to keep in mind however that the bands at 2057cm^{-1} and 2064cm^{-1} , respectively could also account for solvent separated dimers $(\text{NaNCS} \dots \text{NaNCS})_2$ and $(\text{LiNCS} \dots \text{LiNCS})_2$ which would be spectroscopically indistinguishable from the monomer species NaNCS and LiNCS .

Therefore, for instance for sodium thiocyanate solutions any calculation of formation constants based on relations as $A_{2057}^0 = \epsilon_p \ell c_p$ and $A_{2040}^0 = \epsilon_q \ell c_q$ is destined to fail if out sphere dimers are present. In the above ϵ_p and ϵ_q are the extinction coefficients of the ion-pair and quadrupole respectively, c_p and c_q the corresponding concentrations, ℓ the length of the cell. In other words, even if retained, assumptions as $2\epsilon_p = \epsilon_q$ are correct, the calculated $K_q = c_q/c_p^2$ is going to be void of significance if outersphere dimers are present. This is because, in this case $A_{2040}^0 = \epsilon_q c_q^{\text{contact}}$ and $A_{2057}^0 = \epsilon_p (c_p + c_q^{\text{outersphere}})$. The calculated $K_q = c_q^{\text{contact}} / (c_p + c_q^{\text{outersphere}})^2$ would then become strongly concentration dependent. Presence of solvent separated dimers is consistent with the results

of the ultrasonic analysis of the data given below.

The small bands at 2074cm^{-1} , respectively for sodium thiocyanate and lithium thiocyanate have a less definite interpretation than the ones for the other two bands which has also been confirmed by normal coordinate analysis¹². We tentatively attribute these bands at 2074cm^{-1} and 2086cm^{-1} to triple ions existing at lower concentration than the other species. The latter is suggested by the smallness of the A° 's.

Because of the above considerations, we think that it is safe not to over extend vibrational spectrometry beyond its present capability in trying to calculate formation constants at low permittivities where, because of electrostatic forces larger population of outersphere dimers may exist. The same warning referred to ion pairs, in solvent of intermediate permittivity, was given by some of us in a past work¹⁰. The method may be approximately correct for ion-pairs in aqueous solutions because of its large permittivity, although even in this case for metal (II) sulfates, large concentration of outer species ion pair appear to exist.¹⁴ Accordingly, we have only calculated the concentration dependence of the individual maximum absorbances per unit length of cells l , by fitting the data to cubic polynomials as reported below.

For sodium thiocyanate in THF:

$$A_{2043}^\circ/l = -0.31 + 603.1c + 2187.5c^2 - 8649c^3; r^2 = 0.998$$

$$A_{2057}^\circ/l = 0.1996 + 516.6c + 483c^2 - 4942c^3; r^2 = 0.998$$

$$A_{2074}^\circ/l = 0.0131 - 56.34c + 1195c^2 - 2334c^3; r^2 = 0.999$$

For lithium thiocyanate solutions in THF

$$(A_{2040}^\circ/l) = -0.0006 + 51.980c + 379.80c^2 - 285.95c^3; r^2 = 0.99999$$

$$(A_{2064}^0/\rho) = -0.252 + 1610.7c + 5395.9c^2 + 13,490c^3; r^2 = 0.9987$$

$$A_{2086}^0/\rho = 0.1170 - 17.480c_0^2 + 1254.4c^2 - 3320.8c^3; r^2 = 0.9925$$

The above expressions have been calculated by non-linear regression giving 50% statistical weight to the origin. It is noteworthy that the bands at 2043cm^{-1} and 2084cm^{-1} for sodium thiocyanate and lithium thiocyanate solutions may also be expressed as simple linear functions of c with an almost comparable determination coefficient r^2 (dashed lines in Fig. 7) and Fig. 8.

For sodium thiocyanate in THF:

$$A_{2043}^0/\rho = -0.34 + 714.2c; r^2 = 0.997$$

For lithium thiocyanate in THF:

$$A_{2064}^0/\rho = 3.08 + 111.1c; r^2 = 0.9948$$

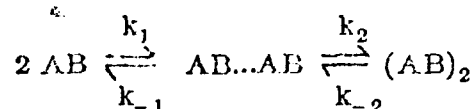
From the analysis of the IR-spectra it would appear therefore that contact dimers are the dominant species for sodium thiocyanate in THF with an almost comparable amount of "spectroscopically" free monomers (free ion-pairs and outersphere dimers). On the contrary for lithium thiocyanate in THF, the latter two species appear as the dominant species. This is in line with the relative solvation tendencies of Li^+ vs. Na^+ ions.

b) Ultrasonic Spectra

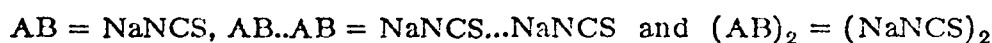
The ultrasonic spectra and the data collected in Table II for sodium thiocyanate in THF can now be interpreted on the basis of the structural information gathered through the IR-spectra. Simple concentration distribution calculations of the various species present in THF with reasonable formation constant parameters as $K_p = 10^8\text{M}^{-1}$, $K_T = 10^2\text{M}^{-1}$ and $K_q = 10\text{M}^{-1}$ (for the ion pair, triple and quadruple formation constants) reveal that in the concentration range 0.05 to 0.2M the ion pair and quadrupole concentrations are of the same

order of magnitude but that $c_p, c_q \gg c_T$, the triple ion concentration.

It is therefore unlikely that the source of any of the two Debye relaxation processes be due to equilibria involving triple ions. Accordingly, we have interpreted the ultrasonic relaxation spectra for sodium thiocyanate in THF according to the two step dimerization equilibrium



where



The above leads¹⁵ to two relaxation times τ_I and τ_{II} , where

$$\tau_{I,II}^{-1} = 1/2 [S \pm \sqrt{S^2 - 4P}]$$

$$S = \tau_I^{-1} + \tau_{II}^{-1} = 4k_1(AB) + k_{-1} + k_2 + k_{-2}$$

$$P = \tau_I^{-1} \times \tau_{II}^{-1} = 4k_1(AB)(k_2 + k_{-2}) + k_{-1}k_{-2}$$

and

$$\tau_I^{-1} = 2\pi f_I, \tau_{II}^{-1} = 2\pi f_{II}.$$

Assuming as a first approximation $AB \approx c$, the stoichiometric concentration, Fig. 9A and Fig. 9B have been constructed.

Linear regression of S vs c gives slope 1.37×10^9 , Int = 3.55×10^8 $r^2 = 0.96$

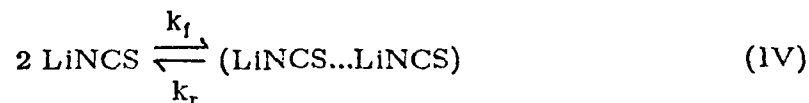
Linear regression of P vs c gives (Slope)' = 1.94×10^{17} (Int)' = 1.86×10^{15} , $r^2 = 0.94$, from which the four kinetic rate constants k_1, k_{-1}, k_2, k_{-2} the formation constants $K_1 = k_1/k_{-1}$, $K_2 = k_2/k_{-2}$ and the dimerization constant $K_q = K_1(1+K_2)$ have been calculated (Table III).

A second approximation has been performed using $K_q = 20M^{-1}$ to calculate $c_p = (AB)$.

The new sequence gives Slope = 6.74×10^9 , Int = 2.02×10^8 , $r^2 = 0.93$ for S vs c, but (Slope)' = 9.49×10^{17} , (Int)' ≈ 0 , $r^2 = 0.90$ for P vs c making impossible further progress without a reliable figure for K_1 .

For lithium thiocyanate in THF, a single Debye process suffices to interpret the ultrasonic relaxation data. The infrared data indicate that the contact species $(\text{LiNCS})_2$ are in minor concentration (as well as the assigned triple ion species), the major species being the "spectroscopically free" LiNCS pair. The latter maybe a combination of LiNCS and (LiNCS...LiNCS) species.

Consequently we have interpreted the ultrasonic spectra for lithium thiocyanate in THF as due to the process



where the product of the reaction maybe mainly (LiNCS...LiNCS) with a minor percentage of contact $(\text{LiNCS})_2$. Both species will be symbolized here as (LiNCS...LiNCS). Notice in fact from Table II that the visible relaxation frequency for lithium thiocyanate solutions 0.1M ($f_r = 60\text{MHz}$) is comparable with $f_1 = 70 \text{ MHz}$ for sodium thiocyanate solutions 0.1M, whereas $f_{II} = 7\text{MHz}$. Scheme IV, leads to the relation¹⁶

$$\tau^{-1} = 4 k_f(\text{LiNCS}) + k_r = 4 k_f(\text{AB}) + k_r \quad (\text{V})$$

with

$$K_1 = \left(\frac{(\text{AB})_2}{(\text{AB})^2} \right) = k_f/k_r; \quad (\text{AB})_2 = (\text{LiNCS} \cdots \text{LiNCS})$$

By calling in zeroth approximation $(\text{AB}) = c$, linear regression of τ^{-1} vs c gives $r^2 = 0.97$, slope = 1.96×10^9 , Int = 1.85×10^8 , from which one calculates $k_f = 4.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_r = 1.85 \times 10^8 \text{ s}^{-1}$, $K_1 = 2.65 \text{ M}^{-1}$. (Fig10)

A series of successive approximations is started with the initial $K_1 = 2.6M^{-1}$. After seven approximations convergence is obtained with $K_1 = 6.6M^{-1}$, $k_f = 9.9 \times 10^8 M^{-1}s^{-1}$, $k_r = 1.5 \times 10^8 s^{-1}$.

Notice that the zeroth approximation $k_f = 4.9 \times 10^8 M^{-1}s^{-1}$ is comparable with the value of $k_f = 3.4 \times 10^8 M^{-1}s^{-1}$ calculated for sodium thiocyanate in THF, reinforcing the above interpretation of the ultrasonic relaxation of lithium thiocyanate leading mainly to outersphere dimers.

Conclusions

The combination of vibrational spectrometry and ultrasonic spectrometry in electrolyte solutions of low permittivity, leads to complementary information of invaluable importance in the interpretation of the relaxation spectra by ultrasonics. Instead of guessing the species participating the chemical equilibria being disturbed by the sound wave, one has indication of their presence by infrared spectra in a comparable concentration range. On the other hand, as any other method, vibrational spectra seem to have limitations in their apparent inability to distinguish between "free species" and "solvent separated species" leading to interpretation errors if one ignores the possible presence of the latter ones.

Work is now in progress with other lithium electrolytes more likely to be employed in solutions used for battery construction.

Acknowledgment

The authors wish to thank the Army Office of Scientific Research, Durham, North Carolina for their generous support through Grant No. DAAG-29-85-K00 51.

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Table 1

Calculated infrared parameters from fitting the digitized infrared spectra to the Gaussian-Lorentzian product function:

$$A = \sum_j A_j^0 \left[\exp \left(- \frac{(\bar{\nu} - \bar{\nu}_j)^2}{2\sigma_j^2} \right) \right] \left[1 + \frac{(\bar{\nu} - \bar{\nu}_j)^2}{\sigma_j^2} \right]^{-1}$$

with $\sigma_j = (\Delta\nu_j)_{1/2}$, for NaSCN and LiSCN in THF.

NaSCN*

C,M	l, mm	A_{2043}^0	$\bar{\nu}_{2043}$	$(\Delta\nu)_{1/2}$	A_{2057}^0	$\bar{\nu}_{2057}$	$(\Delta\nu)_{1/2}$	A_{2074}^0	$\bar{\nu}_{2074}$	$(\Delta\nu)_{1/2}$
0.198	0.057	0.79	2043.5	13	0.47	2057	13	0.10	2074	13
0.148	0.057	0.60	2043	13	0.42	2056	13	0.06	2074	13
0.103	0.050	0.40	2042.5	13	0.25	2057	13	0.02	2074	13
0.050	0.051	0.17	2042	13	0.14	2056.5	13	0.005	2074	13
0.025	0.059	0.080	2042	13	0.087	2057	13	--	--	--

LiSCN*

C,M	l(mm)	A_{2040}^0	$\bar{\nu}_{2040}$	$(\Delta\nu)_{1/2}$	A_{2064}^0	$\bar{\nu}_{2064}$	$(\Delta\nu)_{1/2}$	A_{2086}^0	$\bar{\nu}_{2086}$	$(\Delta\nu)_{1/2}$
0.268	0.056	0.20	2038	14	1.70	2065	14	0.12	2088	14
0.210	0.056	0.14	2040	14	1.26	2065	14	0.12	2086	14
0.100	0.057	0.05	2040	14	0.67	2064	14	0.04	2086	14
0.066	0.061	0.03	2040	13	0.58	2063	13	0.015	2086	13
0.042	0.056	0.016	2040	13	0.29	2064	13	0.018	2086	13

* $\bar{\nu}_j$ and $(\Delta\nu_j)_{1/2}$ are expressed in cm^{-1}

Table 2

Ultrasonic relaxation parameters and sound velocities for NaSCN and LiSCN in THF at $t=25^{\circ}\text{C}$

NaSCN

C (M)	$\mu_I \times 10^5$ --	f_I (MHz)	$\mu_{II} \times 10^5$ --	f_{II} (MHz)	$B \times 10^{17}$ (cm^{-1}s^2)	$u \times 10^{-5}$ (cm s^{-1})
0.20	315	90	40	12	124	1.289
0.158	260	80	35	10	124	1.304
0.11	210	70	15	7	126	1.284
0.056	95	65	10	6	130	1.201

LiSCN

0.10	370	60			112	1.282
0.066	140	50			122	1.279
0.042	150	45			126	1.283
0.024	85	35			124	1.283

Table 3

Rate constants and equilibrium constants for the dimerization of NaSCN in THF according to the scheme

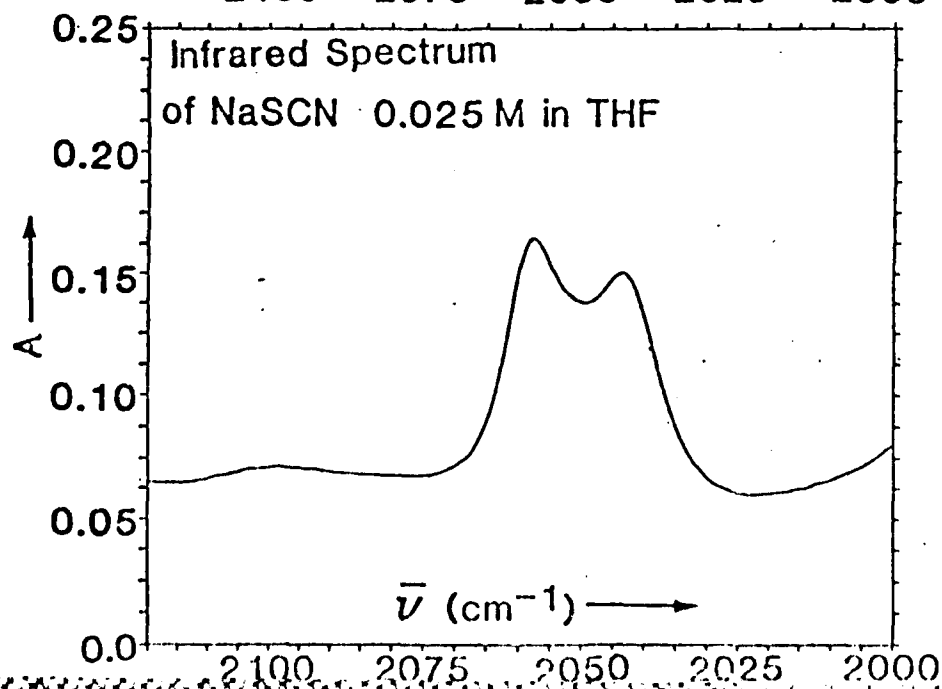
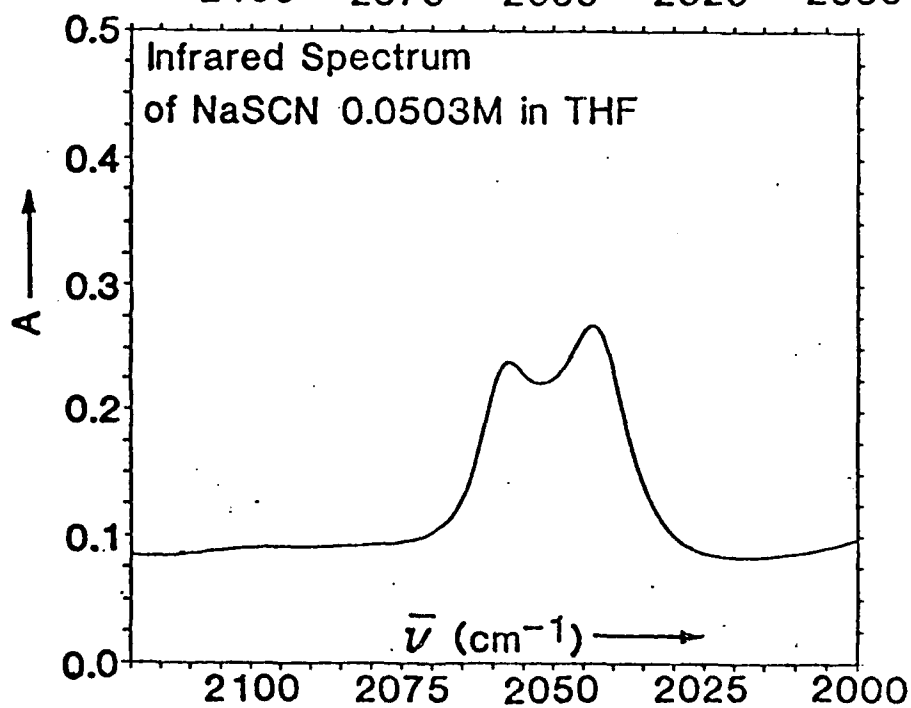
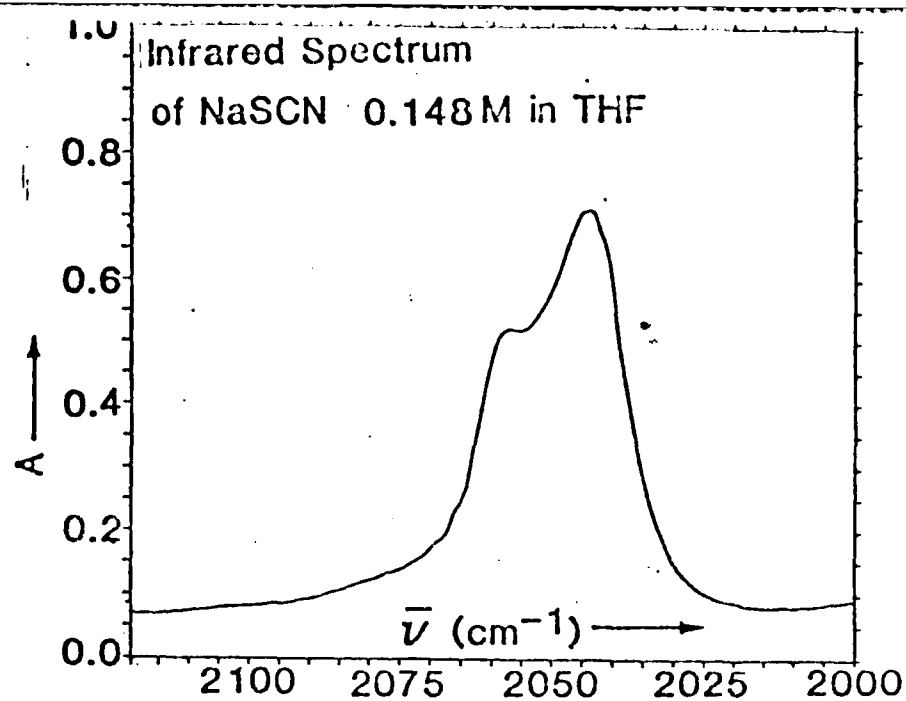
$$2\text{NaSCN} \xrightleftharpoons[k_{-1}]{k_1} (\text{NaNCS} \cdots \text{NaNCS}) \xrightleftharpoons[k_{-2}]{k_2} (\text{NaNCS})_2$$

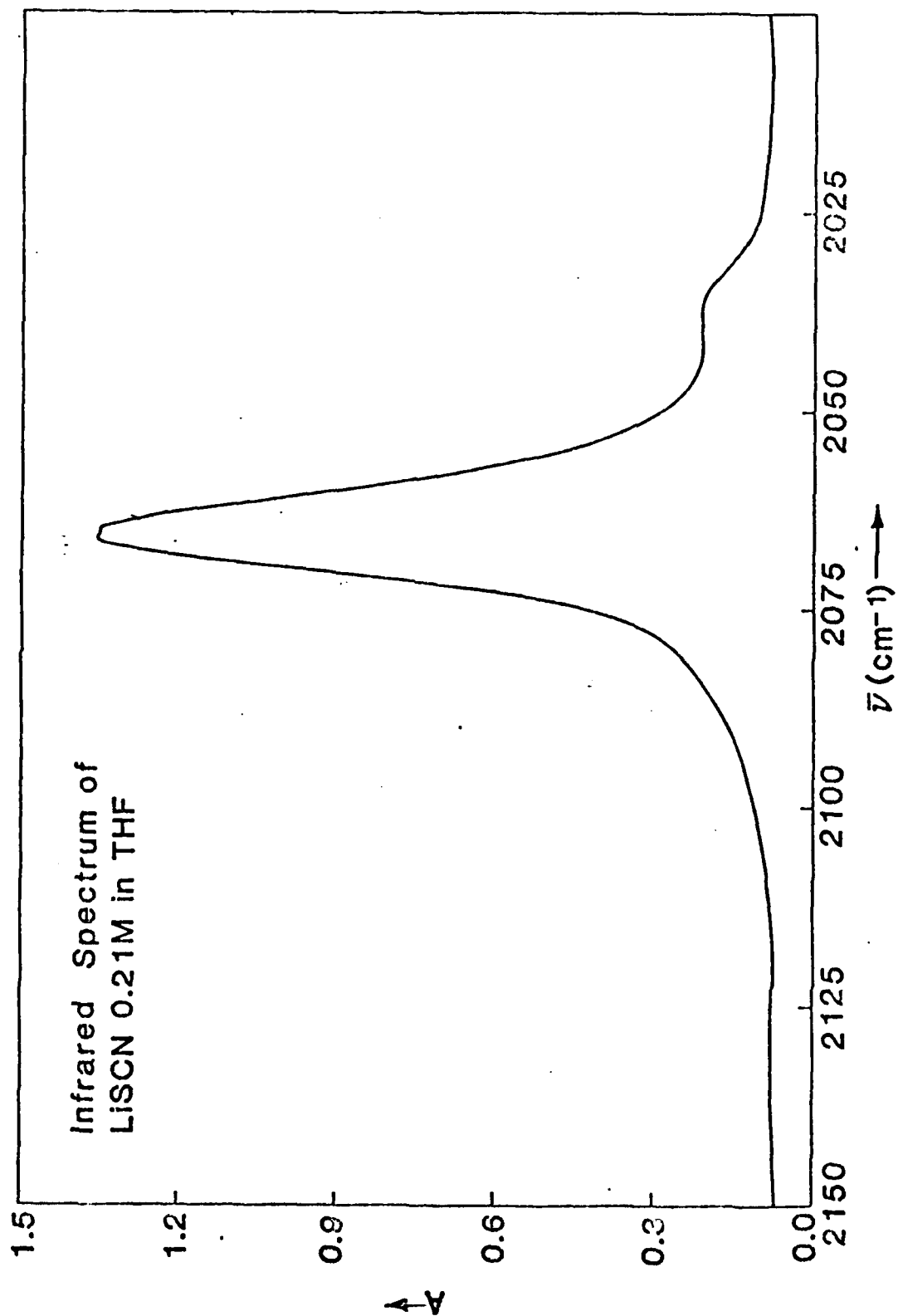
1st appt. $(\text{NaNCS}) = c$

$k_1(\text{M}^{-1}\text{s}^{-1})$	$= 3.4_3 \times 10^8$
$k_{-1}(\text{s}^{-1})$	$= 2.1_3 \times 10^8$
$K_1(\text{M}^{-1})$	$= 1.6$
$k_2(\text{s}^{-1})$	$= 1.3_3 \times 10^8$
$k_{-2}(\text{s}^{-1})$	$= 8.7 \times 10^6$
K_2	$= 15.3$
$K_q = K_1(1 + K_2)(\text{M}^{-1})$	$= 26.1$

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Digitized Infrared Spectrum for
NaSCN 0.198 M in THF

Solid line is the sum of three
Gaussian -Lorentzian product functions:

$$A = \sum_i A_i^0 \exp \left[-\frac{(\bar{\nu} - \bar{\nu}_i)^2}{2\sigma_i^2} \right] \left[1 + \frac{(\bar{\nu} - \bar{\nu}_i)^2}{\sigma_i^2} \right]^{-1}$$

Parameters:

$$\bar{\nu}_1 = 2043.5 \text{ cm}^{-1}$$

$$A_1^0 = 0.79$$

$$\bar{\nu}_2 = 2057 \text{ cm}^{-1}$$

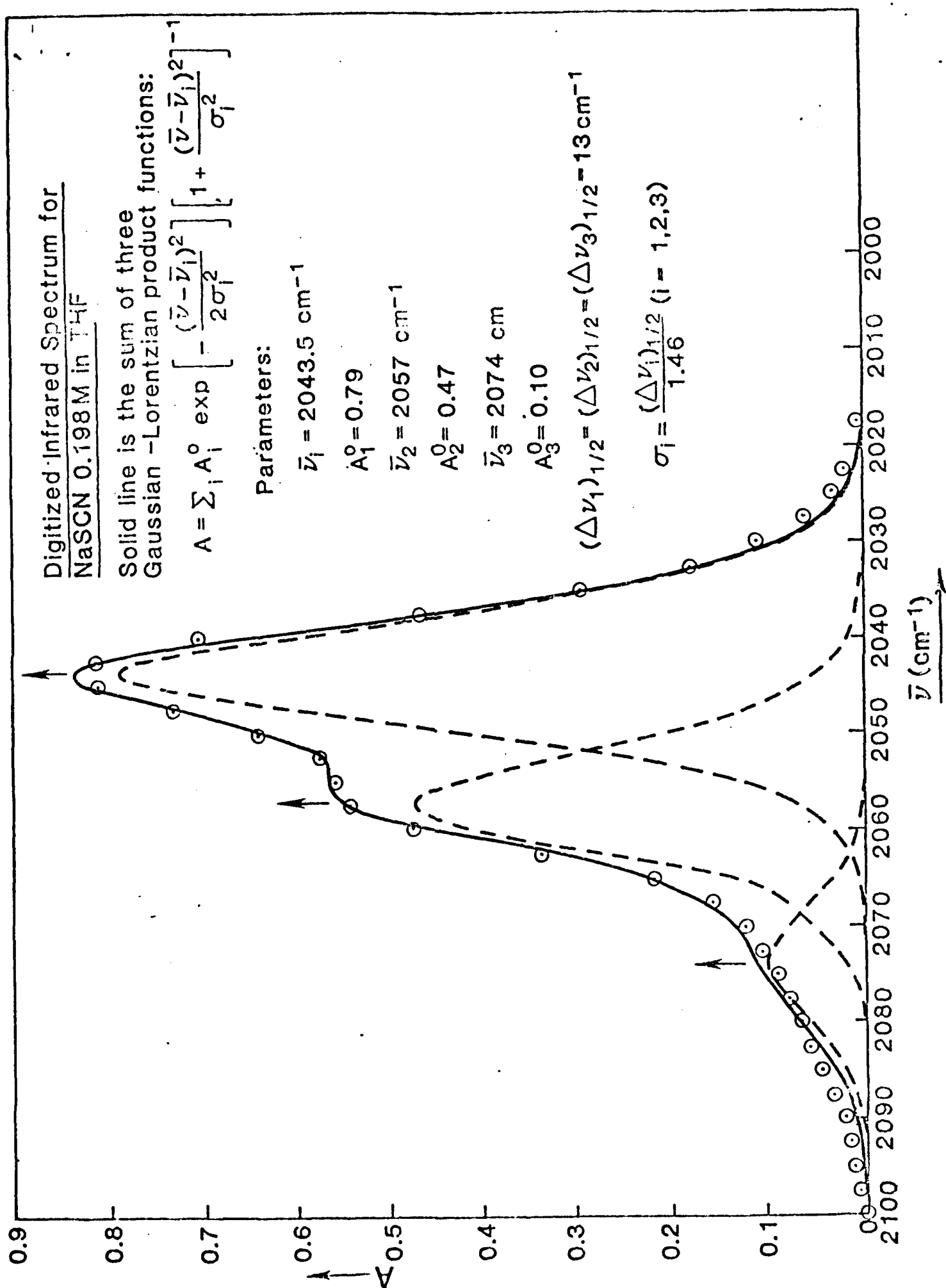
$$A_2^0 = 0.47$$

$$\bar{\nu}_3 = 2074 \text{ cm}^{-1}$$

$$A_3^0 = 0.10$$

$$(\Delta\nu_1)_{1/2} = (\Delta\nu_2)_{1/2} = (\Delta\nu_3)_{1/2} = 13 \text{ cm}^{-1}$$

$$\sigma_i = \frac{(\Delta\nu_i)_{1/2}}{1.46} \quad (i = 1, 2, 3)$$



Digitized Infrared Spectrum for

LiSCN 0.21M in THF

Solid line is the sum of three
Gaussian -Lorentzian product functions:

$$A = \sum_i A_i^0 \exp \left[-\frac{(\bar{\nu} - \bar{\nu}_i)^2}{2\sigma_i^2} \right] \left[1 + \frac{(\bar{\nu} - \bar{\nu}_i)^2}{\sigma_i^2} \right]^{-1}$$

Parameters:

$$\bar{\nu}_1 = 2040 \text{ cm}^{-1}$$

$$A_1^0 = 0.14$$

$$\bar{\nu}_2 = 2065 \text{ cm}^{-1}$$

$$A_2^0 = 1.26$$

$$\bar{\nu}_3 = 2086 \text{ cm}^{-1}$$

$$A_3^0 = 0.12$$

$$(\Delta\nu_i)_{1/2} = 14 \text{ cm}^{-1} (i = 1, 2, 3)$$

$$\sigma_i = \frac{(\Delta\nu_i)_{1/2}}{1.46}$$

↑

1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0

↑

↑

↑

2110 2100 2090 2080 2070 2060 2050 2040 2030 2020 2010 2000

$\bar{\nu} \text{ (cm}^{-1}\text{)}$

NaSCN 0.158M in THF

$t = 25^{\circ}\text{C}$

$$\mu_{\text{I}} = 260 \times 10^{-5}$$

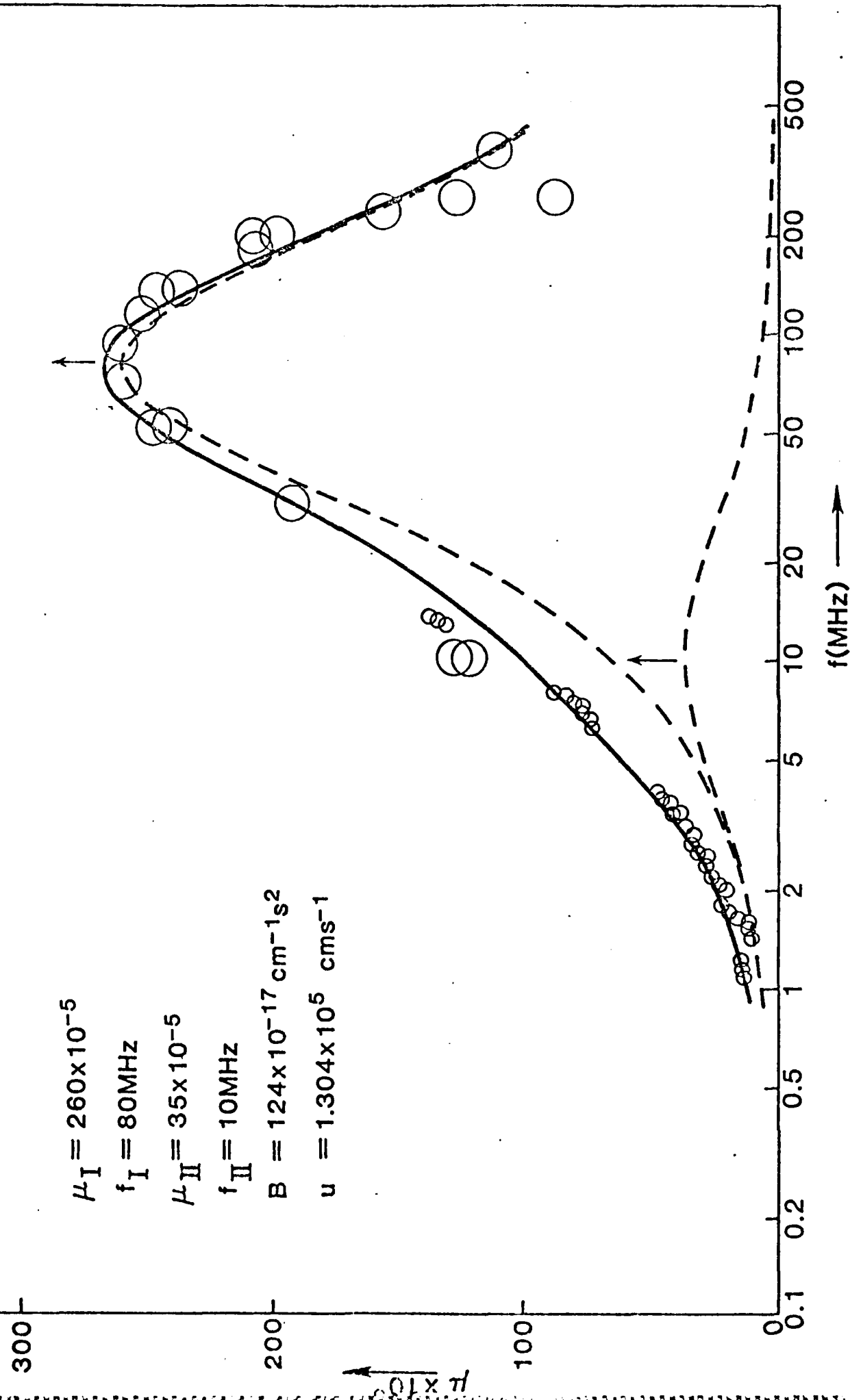
$$f_{\text{I}} = 80 \text{ MHz}$$

$$\mu_{\text{II}} = 35 \times 10^{-5}$$

$$f_{\text{II}} = 10 \text{ MHz}$$

$$B = 124 \times 10^{-17} \text{ cm}^{-1} \text{ s}^2$$

$$u = 1.304 \times 10^5 \text{ cm s}^{-1}$$



LiSCN 0.10M in THF

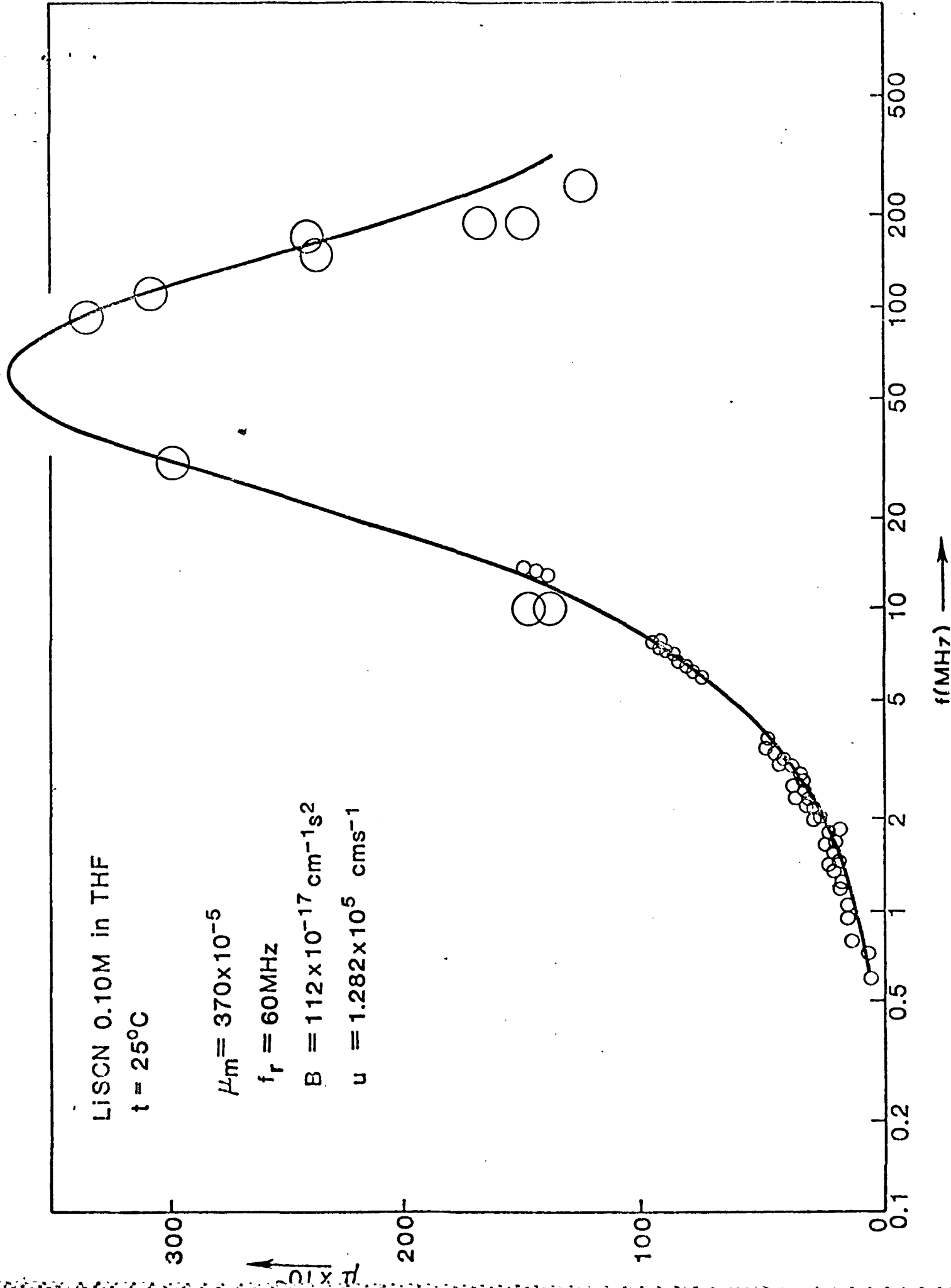
$t = 25^{\circ}\text{C}$

$$\mu_m = 370 \times 10^{-5}$$

$$f_r = 60 \text{ MHz}$$

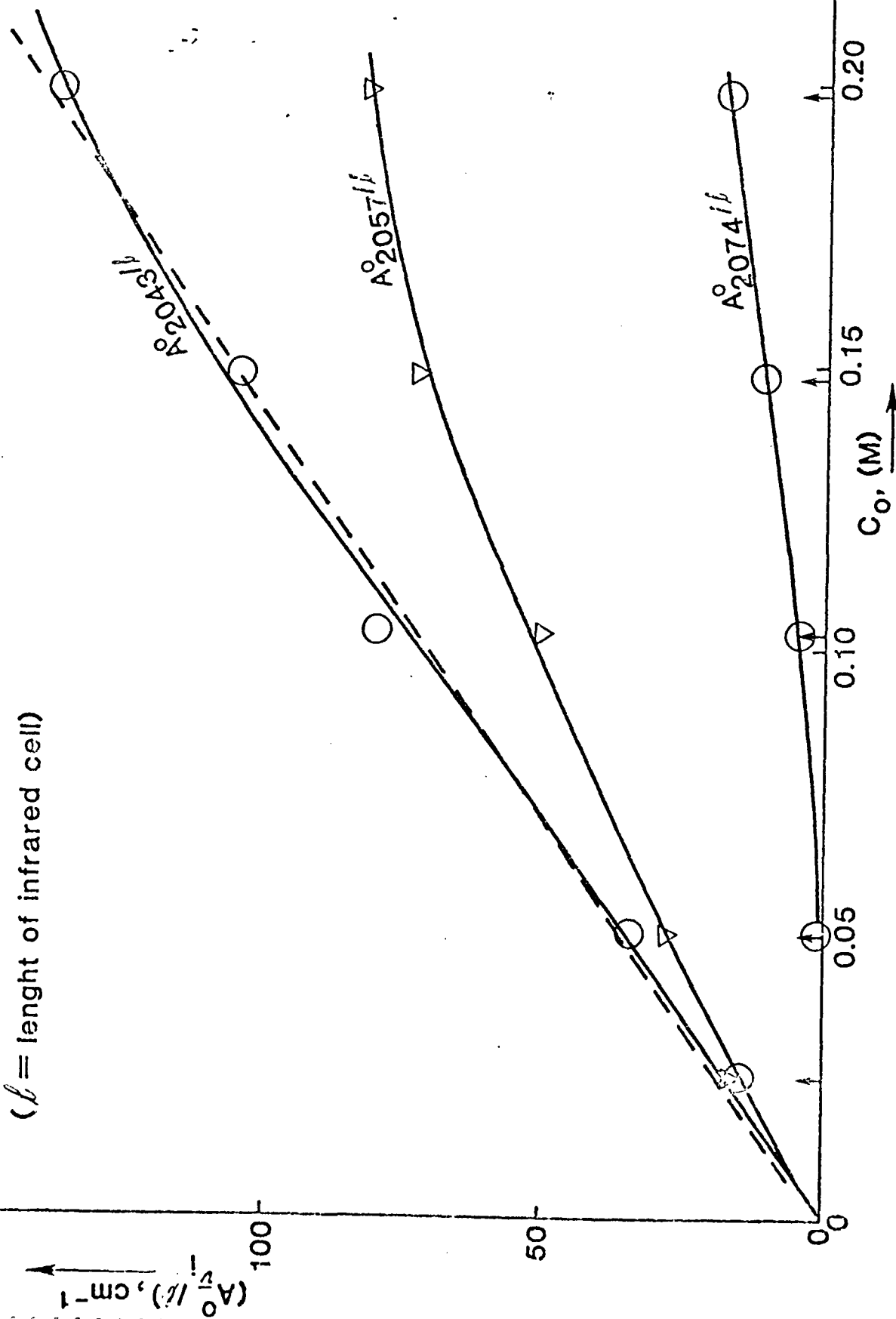
$$B = 112 \times 10^{-17} \text{ cm}^{-1} \text{ s}^2$$

$$u = 1.282 \times 10^5 \text{ cm s}^{-1}$$



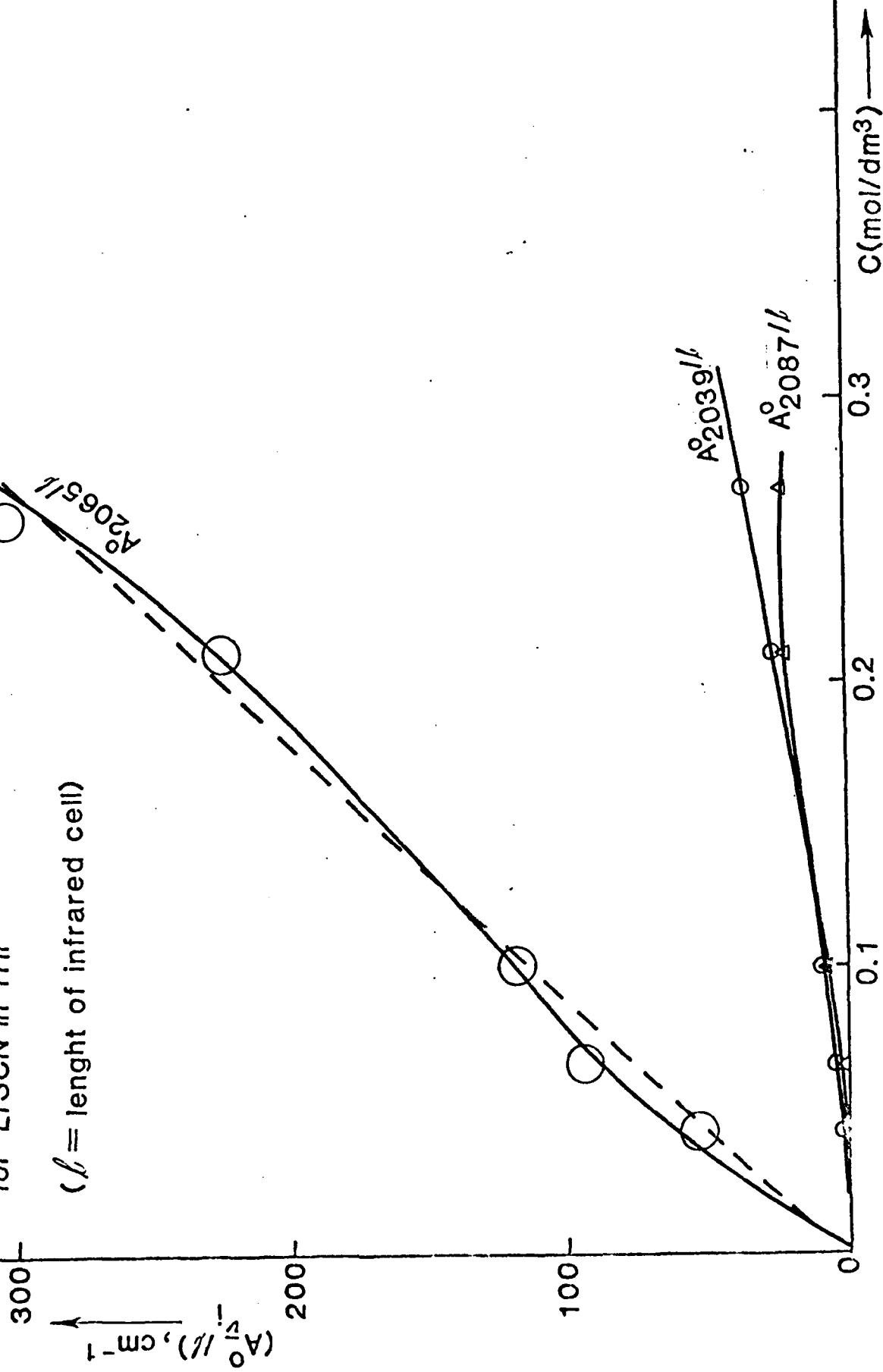
Absorbances per unit length $A_{\nu_i}^0/l$
of the Gaussian Lorentzian
functions vs. concentration
for NaSCN in THF

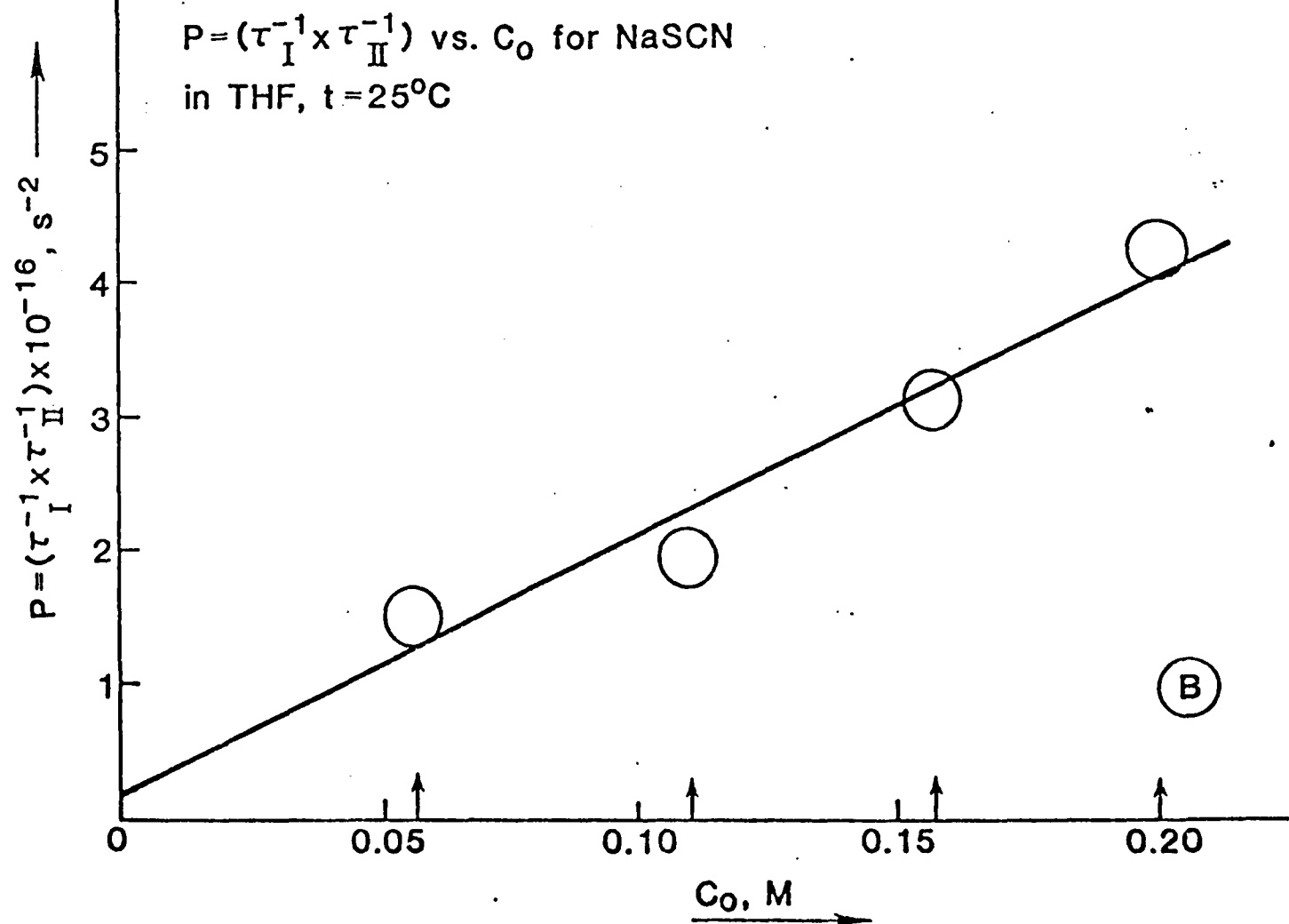
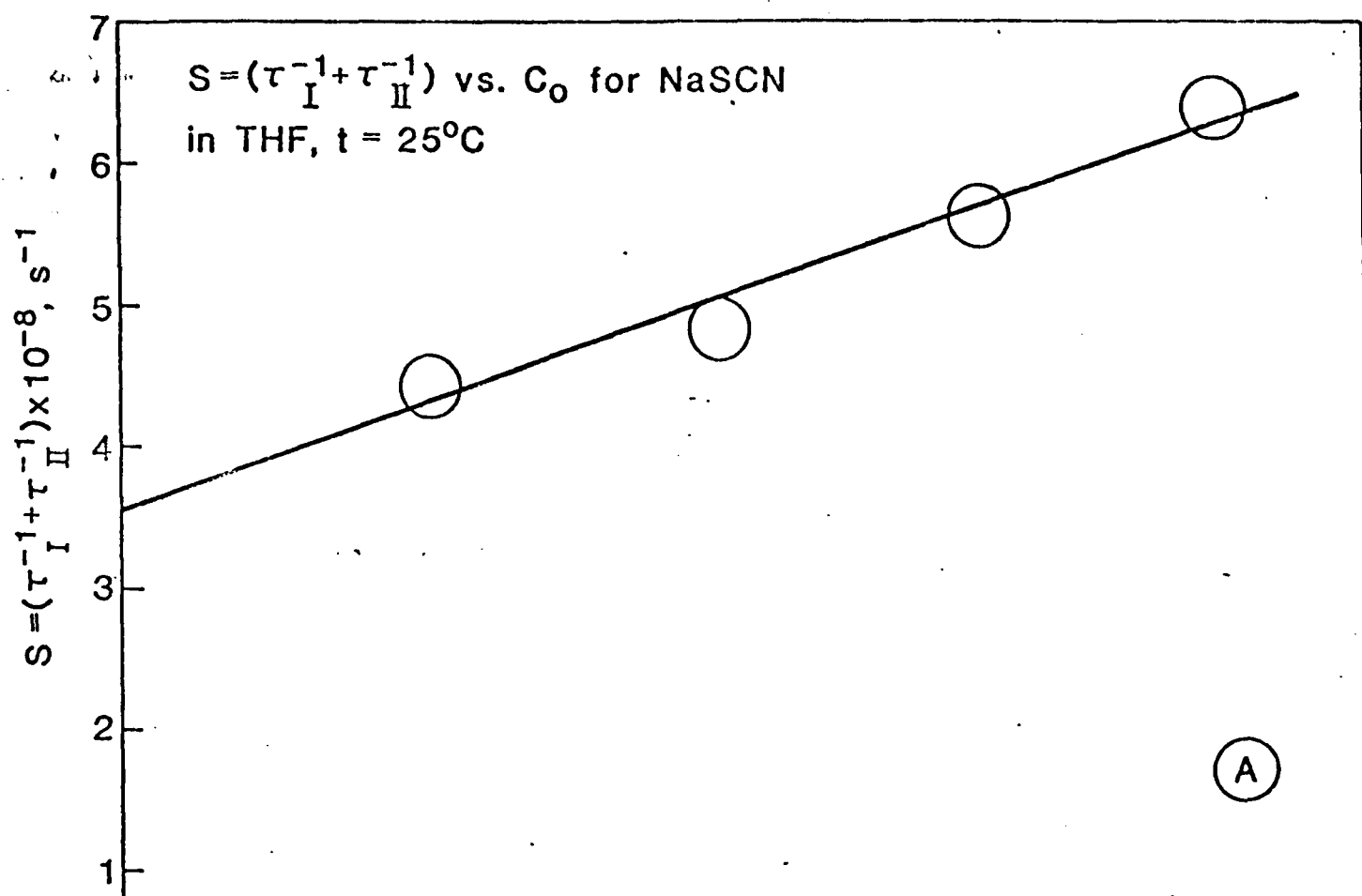
(l = length of infrared cell)



Absorbances per unit length $A_{\nu_i}^0/l$
of the Gaussian-Lorentzian
functions vs. concentration
for LiSCN in THF

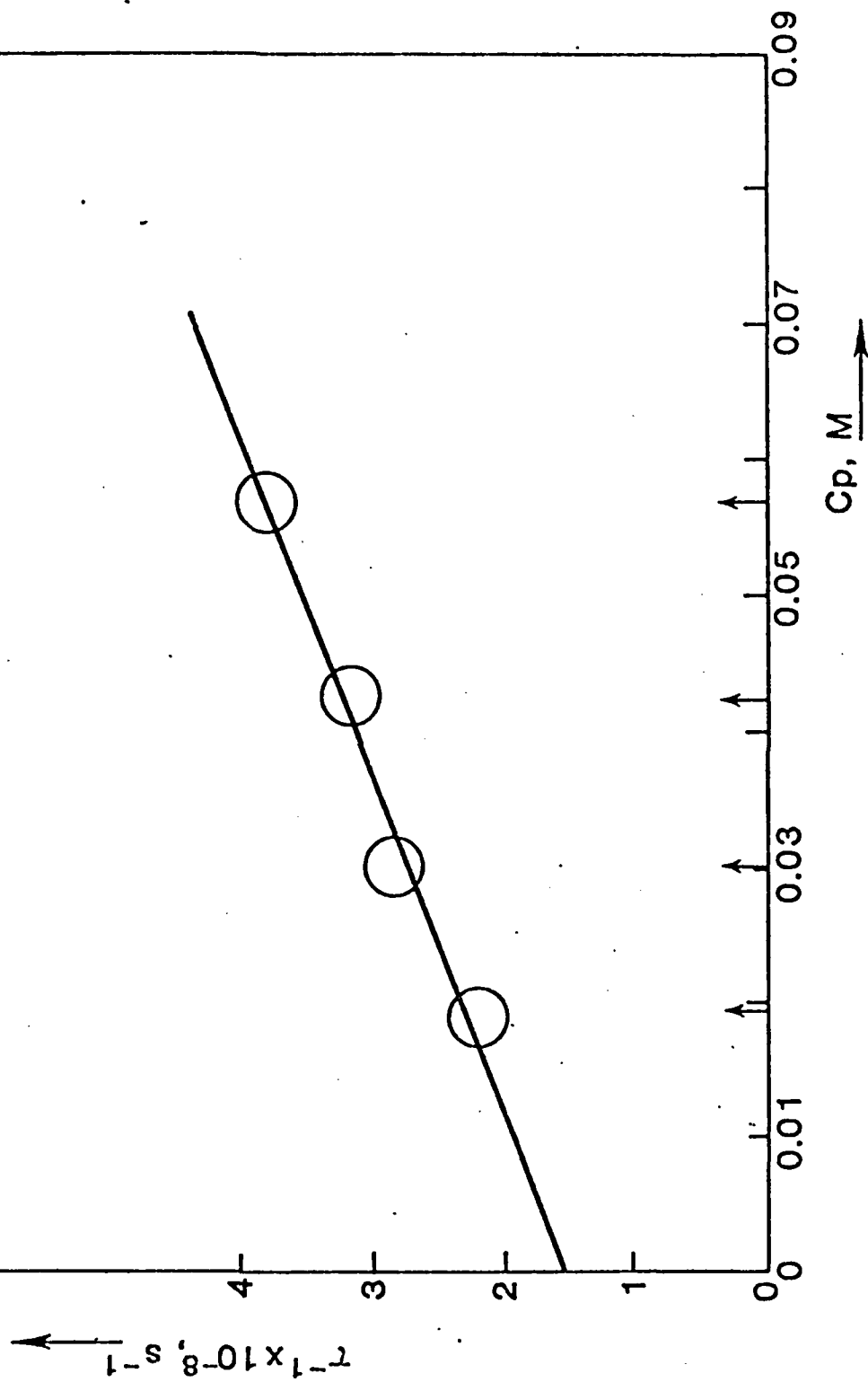
(l = length of infrared cell)





τ^{-1} vs. Cp for LiSCN in THF at $t = 25^\circ\text{C}$

$$Cp = \frac{-1 + \sqrt{1 + 8KqCo}}{4Kq}$$



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